

# Softening of ultra-nanocrystalline diamond at low grain sizes

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Ultra-nanocrystalline diamond is a polycrystalline material, having crystalline diamond grains of sizes in the nanometer regime. We study the structure and mechanical properties of this material as a function of the average grain size, employing atomistic simulations. From the calculated elastic constants and the estimated hardness, we observe softening of the material as the size of its grains decreases. We attribute the observed softening to the enhanced fraction of interfacial atoms as the average grain size becomes smaller. We provide a fitting formula for the scaling of the cohesive energy and bulk modulus with respect to the average grain size. We find that they both scale as quadratic polynomials of the inverse grain size. Our formulae yield correct values for bulk diamond in the limit of large grain sizes.

Keywords: Nanocrystalline materials; carbon & graphite; hardness.

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## I. INTRODUCTION

As most ordinary solids are polycrystalline, the dependence of mechanical and other properties on the size of their grains is a question of fundamental interest for materials science<sup>1</sup>. The hardness of polycrystalline metals increases with decreasing grain size, in accordance to the Hall-Petch law: their yield stress is a linear function of  $d^{-n}$ , where  $d$  is the average grain size and  $n > 0$ . Mechanical load beyond the elastic regime is mostly undertaken by dislocations, and plastic deformation usually involves dislocation motion. By introducing more grain boundary area in the material, when grains become smaller, the motion of dislocations is impeded and dislocations tend to pile up near grain boundaries. This in turn yields harder materials<sup>2,3</sup>.

On the other hand, when the grain size reaches the nanometer range, several metals have been found to exhibit a so-called “reverse Hall-Petch effect”, and become softer at smaller grain sizes<sup>4,5</sup>. The presence of dislocations no longer governs the mechanical response on this regime. As the fraction of atoms residing on grain boundaries increases with decreasing grain size, any external mechanical load will be primarily undertaken by sliding along grain boundaries<sup>4,6,7,8,9</sup>. The interplay between these bulk- and grain-boundary-related mechanisms of plasticity can result to an optimum size of the grains, for which the material is strongest<sup>10,11</sup>. This size is of the order of 10-15 nm for Copper<sup>12</sup>. Contrary to these studies for metals, very few workers have addressed the dependence of mechanical properties on the grain size for nanocrystalline semiconductors or insulators. Examples include a theoretical observation of higher creep rates at

smaller grain sizes for nanocrystalline Si<sup>9</sup> or an experimental observation of a maximum strength for an intermediate grain size in BN nanocomposites<sup>13</sup>.

Several pioneering works have dealt with the mechanical properties of nanocrystalline semiconductors and insulators, like Si<sup>9,14</sup> and SiC<sup>15</sup>. In the present work, we take one step further and investigate the dependence of the mechanical properties on the average grain size in ultra-nanocrystalline diamond (UNCD). C forms extremely strong and directional bonds, while, at the same time, the availability of  $sp^2$  and  $sp^1$  hybridizations allows for the presence of non-defective under-coordinated atoms. This results in lower relative grain-boundary energies compared to other group-IV elements<sup>16</sup>. It is then expected that the difference between the strengths of inter- and intra-grain bonds should be larger in polycrystalline diamond compared to other polycrystalline materials. For this reason, UNCD can serve as a prototype for the mechanical properties of nanocrystalline ceramics.

Ultra-nanocrystalline diamond (UNCD) is a polycrystalline carbon-based material, having grains a few nanometers big<sup>17</sup>. It is a low-cost material with a potential for a wide range of applications due to its unique mechanical and electronic properties<sup>18</sup>; in addition, its properties can be tailored with appropriate doping<sup>19</sup>. Despite the strong directional C-C bonds, resulting in inhomogeneity at the atomic scale, the material can be considered as isotropic at larger scales, as no particular orientation for the grain boundaries in UNCD seems to be favoured in the experiment<sup>17</sup>. Theoretical calculations show that the grain boundary energies have a weak dependence on the orientation<sup>20</sup>, as do the energies of the interfaces between amorphous C and diamond<sup>21</sup>. Sizes of grains were found to have a broad distribution, with

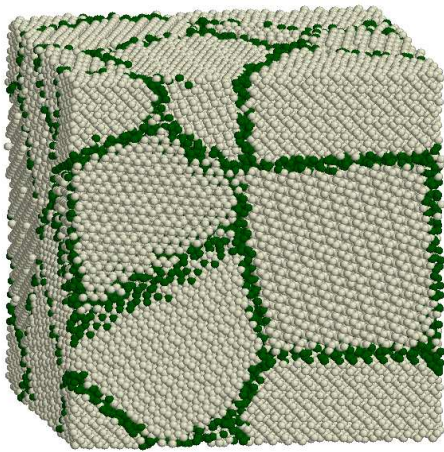


FIG. 1: One of the UNCD samples used in the simulations. The system contains eight grains, with average grain diameter equal to 4.4 nm and contains 116941 atoms in total. Atoms that have less than four neighbors, or deviate significantly from the tetrahedral geometry, are shown in darker color.

an average of about 3 nm and most grains being between 2 and 5 nm<sup>17</sup>. The properties of the material can be tailored by modifying the dopand concentration or the preparation conditions<sup>22,23</sup>.

## II. COMPUTATIONAL METHOD

Theoretical modelling of the mechanical properties of UNCD has only been made possible so far by employing either small clusters<sup>24</sup> or infinite rods<sup>25,26</sup>. Here, we present a fully three-dimensional, computer-generated atomistic model of UNCD, having grains of different sizes separated by random grain boundaries. The simulations were performed using a continuous-space Monte Carlo method. We employ the many-body potential of Tersoff<sup>27</sup>. The choice of the empirical potential is important; for example, different potentials give different responses in Si under large pressures<sup>28</sup>. The Tersoff potential used here provides a very good description of the structure and energetics for a wide range of carbon-based materials<sup>29,30</sup>. This method, although considerably demanding computationally, allows for great statistical accuracy, as it is possible to have samples at full thermodynamic equilibrium. Such an accuracy is necessary due to the many different possible hybridizations of C atoms. In addition, a reliable calculation of mechanical properties requires a fully relaxed structure. Residual stress can affect the mechanical properties, especially in nanocrystalline materials. The supercells we use contain up to about 120000 C atoms.

We model ultra-nanocrystalline diamond (UNCD) by a periodic repetition of cubic supercells that consist of eight different regions (grains) each. The number of grains in the unit cell guarantees the absence of artificial interac-

TABLE I: Properties of characteristic UNCD samples at 300K: average grain size ( $d$ , in nm), number of atoms in the simulation cell ( $N$ ), percentage of three-fold atoms in the cell ( $N_3$ , at %), mass density ( $\rho$ , in g/cc), cohesive energy ( $E_{coh}$ , in eV per atom), bulk modulus ( $B$ , in GPa), Young's modulus ( $E$ , in GPa) and shear modulus ( $G$ , in GPa). For comparison, the corresponding values for single-crystal diamond, calculated with the same method, are shown in the last line (from Ref.<sup>29</sup>).

$d$	$N$	$N_3$	$\rho$	$E_{coh}$	$B$	$E$	$G$
1.94	9,149	33.6	3.14	-7.00	303	719	325
2.43	18,528	26.4	3.22	-7.06	323	808	373
2.93	33,170	20.5	3.28	-7.11	342	891	418
3.44	53,494	12.0	3.30	-7.10	363	939	439
3.92	81,561	10.2	3.37	-7.14	372	963	451
4.41	116,941	9.12	3.40	-7.15	384	987	461
$\infty$	$\infty$	0.00	3.51	-7.33	443	1,066	485

tions between a grain and its periodic images. The grains have random shapes and sizes, and are filled with atoms in a randomly oriented diamond structure. The method we use is identical to the method used by Schiotz and co-workers to model nanocrystalline copper<sup>4,12</sup>. To achieve a fully equilibrated structure for each grain size, we perform four steps: first, the structure is compressed and equilibrated at constant volume at 300 K, in order to eliminate large void regions near some grain boundaries, that are an artifact of the randomly generated structure. In the second step, we anneal the system at 800 K allowing volume relaxation and quench down to 300 K. Third, we anneal once more, at 1200 K this time, in order to ensure full equilibration. Fourth, we fully relax the structure at 300 K allowing for changes in both volume and shape of the unit cell.

## III. RESULTS

### A. Structure

The relaxed structure for a typical sample is shown in Fig. 1. The grain boundaries are a few atomic diameters wide, in accordance with experiments showing widths of 0.2-0.5 nm<sup>17</sup>. Atoms at the grain boundaries are either three-fold coordinated or form bonds at different lengths or angles from those observed in diamond. The structural and elastic properties for characteristic samples are summarised in Table I. The fraction of the three-fold atoms in the samples is about 1/10 for grain sizes between 3.5 and 4.5 nm; in experiment, it was observed that the fraction of atoms residing at grain boundaries is close to 10% for similar crystallite sizes<sup>17</sup>.

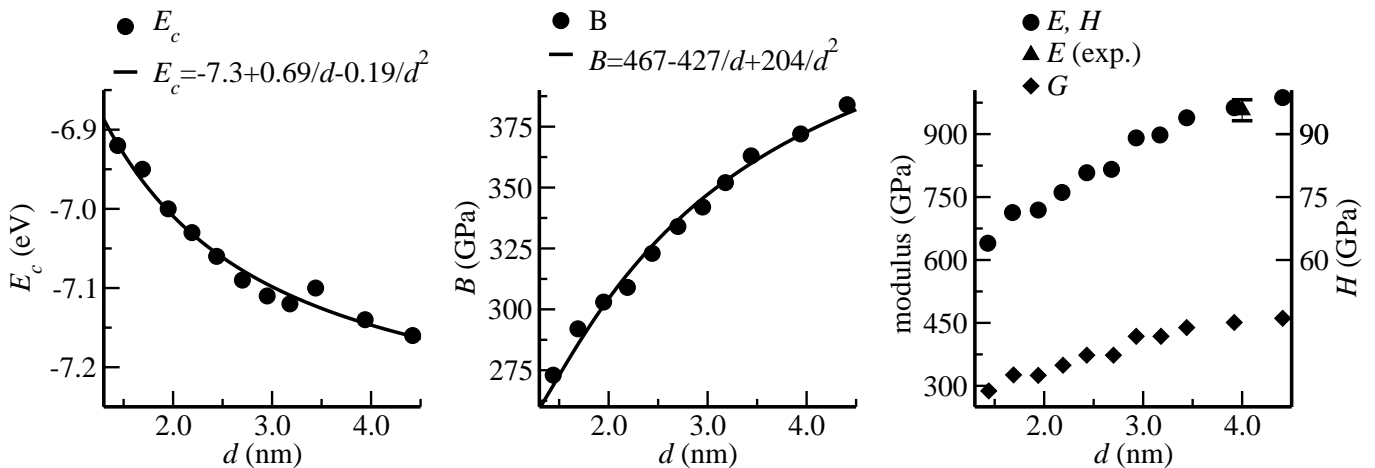


FIG. 2: Cohesive energy (left panel), bulk modulus (center panel), Young's and shear moduli and estimated hardness (right) of UNCD versus the average grain size. The solid lines in the left and central panel are fits to the data. The function used assumes different compressibilities for atoms in the bulk, grain boundaries or edges. In the right panel, the experimental value from Ref.<sup>32</sup> is also shown.

### B. Elastic moduli and estimated hardness

The bulk modulus ( $B$ ) and Young's modulus ( $E$ ) are calculated by applying small hydrostatic and uniaxial deformations to the material, respectively. We find the moduli by fitting a parabola to the thus obtained energy versus strain data. In the case of Young's modulus, we apply load along three mutually perpendicular directions, and take the average. Bulk moduli of UNCD samples are plotted against the average grain size in Fig. 2. They constantly decrease with decreasing grain size, offering a first evidence for softening of the material at small grain sizes. The same behavior is observed through the Young's and shear moduli that are shown in Fig. 2.<sup>39</sup> For the experimentally relevant range of grain sizes, between 3 to 5 nm, UNCD samples are found to have very high elastic moduli, only slightly lower than those of diamond, placing thus UNCD into the family of super-hard materials<sup>31</sup>. The Young's modulus of high-purity UNCD was measured to be  $957 \pm 25$  GPa<sup>32</sup>. This is in excellent agreement with our result of 963 GPa for a grain size of 3.9 nm.

All elastic moduli are found to decrease with decreasing average grain size, indicating softening of the material. This suggests that, in this range of grain sizes, the hardness of the material should also drop with decreasing grain size. Indeed, the hardness of many materials is proportional to the Young's or shear modulus<sup>33</sup>. For nanocrystalline materials, extended defects, like cracks, cannot exist as their lengths are in the micrometer range<sup>34</sup>, rendering the elastic constants good descriptors of hardness. In particular, the hardness of carbon-based materials has been found to be between 10% and 16% of the Young's modulus<sup>35</sup>. This allows us to make a rough estimate for the hardness of UNCD, as being roughly one tenth of its Young's modulus. We use this approximation

to plot the estimated hardness of UNCD as a function of grain size in Fig. 2.

## IV. DISCUSSION

Our results, together with observations for nanocrystalline copper<sup>4</sup>, silicon<sup>9</sup>, and boron nitride<sup>13</sup>, show that softening at small grain sizes can occur in various different nanocrystalline materials. This might be understood considering the relative numbers of atoms near boundaries and in the bulk of grains. These numbers become comparable for grains in the nanometer regime, no matter what the particular chemical composition of the material is. Atoms at grain faces, edges or vortexes, as well as atoms near other discontinuities, will naturally form bonds that are weaker than those formed by atoms in the bulk. Such weaker bonds will then bend or stretch with greater ease, compared to the bonds in the crystalline region. This explains the softening of polycrystalline solids when the grain size is at the nanometer range. For much larger grain sizes, the number of grain-boundary atoms will be negligible compared to the number of bulk atoms; in this regime, the behavior of the material under mechanical load will be characterised mostly by bulk defects, such as dislocations.

To make this picture quantitative, let us divide the atoms in the polycrystalline material into three categories: (a) Atoms deep inside the grains, forming bonds that are roughly identical to those in the single-crystal material. Their number is proportional to  $d^3$ , where  $d$  is the average grain size. (b) Atoms near the grain boundary; these behave similarly to surface or interface atoms. Their number is proportional to  $d^2$ . (c) Atoms near grain boundary edges; these are similar to kink surface atoms, or atoms near dislocation cores. Their number is proportional to  $d$ . Of course, there will be other types of atoms,

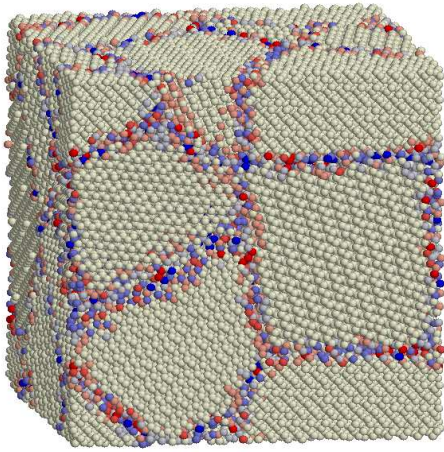


FIG. 3: The UNCD sample shown in Fig. 1, with atoms being colored according to their local bulk moduli: atoms having bulk moduli within 10% of the average value are colored gray. Blue and red color indicate deviation from the average value towards higher or lower values, respectively. Darker colors indicate higher absolute value of the deviation.

like vertex atoms or atoms near topological defects, but their number will be much smaller than the numbers of atoms falling in one of the aforementioned categories. The cohesive energy of the solid will be the sum of the energies of the three different atom types, multiplied by their respective numbers, and divided by the total number of atoms, which is proportional to  $d^3$ . Therefore, the cohesive energy should be described by a function of the form  $E_{coh} = E_0 + a/d + b/d^2$ , where  $a$ , and  $b$  are constants, and  $E_0$  is the cohesive energy of the monocrystalline solid. Indeed, such a function fits our data perfectly, the rms error being less than 0.5%. Moreover,  $E_0$  is found to be -7.31 eV, very close to the calculated cohesive free energy of diamond at 300 K which is -7.33 eV. As  $B$  is proportional to the second derivative of the total energy with respect to the system volume, it can also be decomposed into contributions from bulk, interface and vertex atoms. As shown in Fig. 2, a parametrisation of the form of a quadratic equation in  $1/d$  fits very nicely the results of the simulation. The constant value, 467 GPa, corresponding to the ideal monocrystalline solid, is only 5% off the calculated value for diamond. Such a decomposition of the total bulk modulus to a sum of atomic-level moduli has been used previously, in order to investigate the rigidity of amorphous carbon<sup>30</sup>. Fig. 3, showing the local bulk moduli in the sample, demonstrates the existence of atoms near the grain boundaries having bulk moduli well away from the average value. It is these atoms that contribute to the terms proportional to  $1/d$  and  $1/d^2$  in the function that fits the simulation

data for the bulk modulus.

In this particular example of a nanocrystalline material, under-coordinated atoms may not necessarily be considered to be defects. Carbon atoms are known to exist in several hybridizations, and bonds between two-fold coordinated  $sp^1$  atoms or between three-fold coordinated  $sp^2$  atoms are usually stronger than bonds between four-fold coordinated  $sp^3$  atoms. For example, in amorphous carbon, where all these hybridizations co-exist, it is the failure of bonds between  $sp^3$  atoms that governs the fracture of the material<sup>36</sup>. The ability of carbon to have  $sp^2$  atoms renders grain boundaries in UNCD to be extremely stable<sup>37</sup>. On the other hand, bonds between  $sp^2$  or  $sp^1$  atoms are stabilised by  $p$ -bonding, which is very sensitive to the geometry. As a consequence, local bulk moduli of  $sp^1$  and  $sp^2$  atoms are found to be significantly lower than the bulk moduli of  $sp^3$  atoms<sup>30</sup>. This is demonstrated by the lower bulk modulus of  $sp^2$ -rich amorphous carbon compared to  $sp^3$ -rich one<sup>38</sup>. Here, a similar analysis of some UNCD samples reveals that the average bulk modulus of the three-fold atoms ( $\sim 250$  GPa) is much lower than the average bulk modulus of the four-fold atoms ( $\sim 420$  GPa), which, in turn, predominates the bulk modulus of the sample.

## V. CONCLUSIONS

Using ultra-nanocrystalline diamond (UNCD) as a prototype for a polycrystalline covalent solid with grains at the nanometer regime, we have observed softening of the material as the grain size decreases, in analogy with the reverse Hall-Petch effect observed in nanocrystalline metals. The effect is attributed to the increasing fraction of grain-boundary atoms as the grain size decreasing. A simple quadratic form in  $1/d$ , where  $d$  is the average grain size, suffices to fit the results for both cohesive energy and bulk modulus, while yields the correct values for bulk diamond for large grain sizes. The measured Young's modulus of UNCD is reproduced well by the simulations. Our results provide further evidence that softening at low grain sizes can occur in various kinds of nanocrystalline solids.

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  - <sup>39</sup> The shear moduli,  $G$ , are calculated from the values of  $B$  and  $E$ . For an isotropic material there are only two independent elastic constants; the formula connecting  $B$ ,  $E$  and  $G$  is  $G = \frac{3BE}{9B - E}$ .